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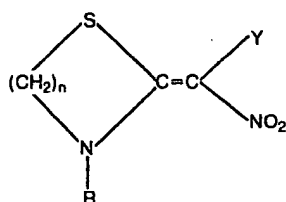
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Process for producing heterocyclic compounds having nitromethylene group as the side chain group.

Disclosed is a process for producing a heterocyclic compound having a nitromethylene group as the side chain, of the formula:



wherein Y represents a hydrogen atom, a halogen atom or a lower alkyl group, R represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkenyl group, an alkynyl group or an acyl group, and n represents an integer of 2, 3 or 4,  
which comprises reacting a 2,2,2-trihalo-1-nitroethane compound with a 1-aminoalkanethiol compound or a 1-N-substituted derivative thereof.

- i -

Process for producing heterocyclic compound having  
nitromethylene group as the side chain group

BACKGROUND OF THE INVENTION

5 This invention relates to a novel process for producing a  
heterocyclic compound having a nitromethylene group as  
the side chain group.

Heterocyclic compounds having a nitromethylene group as  
the side chain group find uses in agricultural chemicals,  
pharmaceuticals or perfumes. For example, Japanese  
10 Unexamined Patent Publication No.151882/1975 proposes  
tetrahydro-2-(nitromethylene)-1,3-thiazines having  
excellent activities as agricultural chemicals such as  
pesticides and acaricides.

15 In the prior art, most of the processes for preparation  
of heterocyclic compounds having a nitromethylene group  
as the side chain employ as the starting material cyclic  
dithiocarbamic acid esters which can easily be  
synthesized and are also highly reactive.

20 For instance, the above Unexamined Patent Publication  
discloses the following process as the process for

preparation of tetrahydro-2-(nitromethylene)-1,3-thiazines.

First, tetrahydro-1,3-thiazine-2-thion is methylated with a methyl halide, the resultant tetrahydro-2-(methylthio)-1,3-thiazine is allowed to react with an alkyl nitro-  
 5 acetate in the presence of zinc ions to give an alkyl nitro(tetrahydro-1,3-thiazine-2-ylidene)acetate, which is then hydrolyzed in the presence of a base, followed by decarboxylation to prepare a desired product of  
 10 tetrahydro-2-(nitromethylene)-1,3-thiazine.

As can be seen from this example, the process for preparation of a heterocyclic compound having a nitromethylene group as the side chain group, using a cyclic dithiocarbamic acid ester as the starting material  
 15 involves the reaction steps which are very lengthy and complicated, and methyl mercaptan which may cause offensive odor is generated in the step of reacting the methylated starting material with an alkyl nitroacetate. Thus, this process cannot necessarily be stated to be  
 20 satisfactory in industrial application.

#### SUMMARY OF THE INVENTION

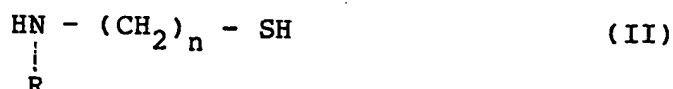
The present inventors have made extensive studies in order to establish a process for producing industrially advantageously a heterocyclic compound having a nitromethylene group as the side chain group. As a result, it  
 25 has now been found that a 2,2,2-trihalo-1-nitroethane compound of the formula (I):



wherein  $\text{X}^1$ ,  $\text{X}^2$  and  $\text{X}^3$  may be the same or different

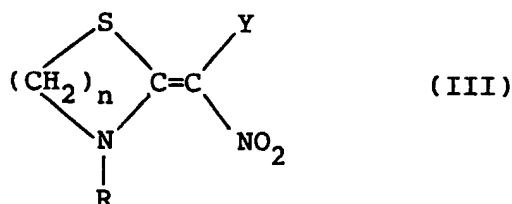
and represent halogen atoms, and Y represents a hydrogen atom, a halogen atom or a lower alkyl group,

5 can be allowed to react with a 1-aminoalkanethiol compound or a 1-N-substituted derivative thereof of the formula (II):



10 wherein R is a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkenyl group, an alkynyl group or an acyl group, and n represents an integer of 2, 3 or 4,

in the presence of a base and in a solvent to produce industrially advantageously a heterocyclic compound having a nitromethylene group as the side chain group, of the formula (III):



15 wherein Y represents a hydrogen atom, a halogen atom or a lower alkyl group, R represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkenyl group, an alkynyl group or an acyl group, and n represents an  
20 integer of 2, 3 or 4,

to accomplish the present invention.

This invention is extremely simplified in the reaction step, as compared with the process of the prior art as

described above, without by-production of methyl mercaptan, which will cause troubles in industrial practice of the process, and the desired product can be also obtained at a high yield.

5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 In the 2,2,2-trihalo-1-nitroethane compound represented by the above formula (I), which is the starting material to be used in this invention, the halogen atoms represented by  $X^1$ ,  $X^2$ ,  $X^3$  and Y may be either the same or different, and they may be any of chlorine, bromine, fluorine and iodine. The lower alkyl group represented by Y may include alkyl groups having 1 to 4 carbon atoms such as methyl, ethyl, propyl and butyl.

15 Examples of the compound (I) are 2,2,2-trihalo-1-nitroethanes such as 2,2,2-trichloro-1-nitroethane, 2-bromo-2,2-dichloro-1-nitroethane, 2-chloro-2,2-dibromo-1-nitroethane, 2,2-dichloro-2-iodo-1-nitroethane, 2-chloro-2,2-diiodo-1-nitroethane, 2,2-dichloro-2-fluoro-1-nitroethane, 2-chloro-2,2-difluoro-1-nitroethane, 2,2-dibromo-2-iodo-1-nitroethane, 2-bromo-2,2-diiodo-1-nitroethane, 2,2-dibromo-2-fluoro-1-nitroethane, 2-bromo-2,2-difluoro-1-nitroethane, 2,2,2-tribromo-1-nitroethane, 2,2,2-triiodo-1-nitroethane, 2,2,2-trifluoro-1-nitroethane, 1-methyl-2,2,2-trichloro-1-nitroethane, 1-ethyl-2,2,2-trichloro-1-nitroethane, 1-methyl-2-bromo-2,2-dichloro-1-nitroethane and 1-ethyl-2-bromo-2,2-dichloro-1-nitroethane; and 1,2,2,2-tetrahalo-1-nitroethanes such as 1,2,2,2-tetrachloro-1-nitroethane, 1-bromo-2,2,2-trichloro-1-nitroethane, 2-bromo-1,2,2-trichloro-1-nitroethane, 1,2-dibromo-2,2-dichloro-1-nitroethane, 2,2-dibromo-1,2-dichloro-1-nitroethane, 1-chloro-2,2,2-tribromo-1-nitroethane, 2-chloro-1,2,2-tribromo-1-nitroethane and 1,2,2,2-tetrabromo-1-nitroethane.

Among them, in view of industrial availability, 2,2,2-trichloro-1-nitroethane, 2,2,2-tribromo-1-nitroethane and 1,2,2,2-tetrachloro-1-nitroethane are particularly useful.

- 5 These 2,2,2-trihalo-1-nitroethane compounds can be readily synthesized according to the process known in the art. For example, in the case of the above-mentioned 2,2,2-trihalo-1-nitroethane, it can be synthesized according to the reaction between a 2,2-dihaloethylene  
10 and a nitronium halide, while in the case of the above-mentioned 1,2,2,2-tetrahalo-1-nitroethane, according to the reaction between a 1,2,2-trihaloethylene, a dinitrogen tetraoxide and a halogen.

- 15 The 1-aminoalkanethiol or its 1-N-substituted derivative thereof represented by the above formula (II), which is the other starting material to be used in this invention, is a commercially available compound.

- Examples of 1-aminoalkanethiol which is the compound (II) wherein R is a hydrogen atom, are 1-amino-2-ethanethiol,  
20 1-amino-3-propanethiol and 1-amino-4-butanethiol.

- The alkyl group represented by R may include alkyl groups having 1 to 12 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. As the cycloalkyl group,  
25 there may be included cycloalkyl groups having 5 to 12 carbon atoms such as cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl and cyclododecyl. As the aralkyl group, there may be employed benzyl group and phenethyl group. Alkenyl  
30 groups may be, for example, those having 3 to 5 carbon atoms such as allyl, butenyl and pentenyl. Further, the alkynyl group may include those having 3 to 5 carbon

atoms such as propargyl, butyl, and pentynyl. The acyl group may include formyl, acetyl, propionyl, butyryl, valeryl, palmitoyl, stearoyl, oleoyl, oxalyl, malonyl, succinyl, benzoyl, toluoyl, salicyloyl, cinamoyl, naphthoyl, phthaloyl, furoyl, methoxycarbonyl, ethoxycarbonyl and propoxycarbonyl.

Typical examples of the 1-N-substituted derivatives of 1-aminoalkanethiol are 1-methylamino-2-ethanethiol, 1-methylamino-3-propanethiol, 1-methylamino-4-butanethiol, 1-ethylamino-2-ethanethiol, 1-ethylamino-3-propanethiol, 1-ethylamino-4-butanethiol, 1-propylamino-2-ethanethiol, 1-propylamino-3-propanethiol, 1-propylamino-4-butanethiol, 1-isopropylamino-3-propanethiol, 1-butylamino-3-propanethiol, 1-pentylamino-3-propanethiol, 1-hexylamino-3-propanethiol, 1-octylamino-3-propanethiol, 1-decylamino-3-propanethiol, 1-dodecylamino-3-propanethiol, 1-cyclohexylamino-2-ethanethiol, 1-cyclohexylamino-3-propanethiol, 1-cyclohexylamino-4-butanethiol, 1-cyclooctylamino-3-propanethiol, 1-cyclo-dodecylamino-3-propanethiol, 1-benzylamino-2-ethanethiol, 1-benzylamino-3-propanethiol, 1-benzylamino-4-butanethiol, 1-allylamino-2-ethanethiol, 1-allylamino-3-propanethiol, 1-allylamino-4-butanethiol, 1-propargylamino-2-ethanethiol, 1-propargylamino-3-propanethiol, 1-N-formyl-2-ethanethiol, 1-N-formyl-3-propanethiol, 1-N-formyl-4-butanethiol, 1-N-acetyl-3-propanethiol, 1-N-acetyl-4-butanethiol, 1-N-propionyl-3-propanethiol, 1-N-butyryl-4-propanethiol, 1-N-oxalyl-3-propanethiol, 1-N-succinyl-3-propanethiol, 1-N-benzoyl-3-propanethiol, 1-N-malonyl-3-propanethiol, 1-N-methoxycarbonyl-3-propanethiol, 1-N-ethoxycarbonyl-3-propanethiol, 1-N-isopropoxycarbonyl-3-propanethiol,

These 1-aminoalkanethiol compounds or 1-N-substituted derivatives thereof may be used in an amount generally in

the range of from 0.5 to 10 moles, preferably from 1 to 5 moles, per mole of the 2,2,2-trihalo-1-nitroethane compound.

Useful bases to be used in this invention are alcoholates  
5 of alkali metals such as sodium methoxide, sodium ethoxide, potassium methoxide or potassium ethoxide; hydroxides of alkali metals such as sodium hydroxide or potassium hydroxide; hydroxides of alkaline earth metals such as calcium hydroxide, barium hydroxide or magnesium  
10 hydroxide. These bases can be used in amounts generally of 3 moles or more, preferably 3 to 6 moles, per mole of the 2,2,2-trihalo-1-nitroethane provided for use.

The reaction in this invention is carried out in a solvent. As the solvent to be provided for use, any  
15 solvent may be useful, so long as it can dissolve both starting materials and the base at the same time and is inert to the reaction. Typical examples of the solvent may include lower aliphatic alcohols such as methanol, ethanol, i-propanol, n-propanol, i-butanol or n-butanol,  
20 water, dimethyl sulfoxide, acetonitrile and dimethylformamide. Among them, it is particularly preferred for industrial practice to employ a lower aliphatic alcohol as the solvent.

In the present invention, it is not necessary to provide  
25 limitations with respect to the method by which a 2,2,2-trihalo-1-nitroethane compound is brought into contact with 1-aminoalkanethiol compound or its 1-N-substituted derivative.

For example, a base may be added into a solution in which  
30 both starting materials are dissolved in a solvent. Alternatively, a 1-aminoalkanethiol compound or its 1-N-substituted derivative may be beforehand reacted with



- a base in a solvent to convert the thiol compound to a thiolate compound, followed by addition of a 2,2,2-trihalo-1-nitroethane compound into the solution thereof. However, a desired compound can be obtained at still  
5 higher efficiency by employment of the method in which a 2,2,2-trihalo-1-nitroethane and a base dissolved in separate solvents are added gradually, sometimes in divided portions, into a solution of a 1-aminoalkanethiol compound or its 1-N-substituted derivative.
- 10 The reaction according to this invention may be carried out at a temperature generally of 100°C or lower, preferably of -10 to 50°C, for 0.5 to 10 hours, preferably 1 to 5 hours.
- Thus, a heterocyclic compound having a nitromethylene  
15 group as the side chain can be obtained at a high yield. For example, when 1-amino-2-ethanethiol or 1-methylamino-2-ethanethiol is used as the 1-aminoalkanethiol compound or its 1-N-substituted derivative, there can be produced thiazolidines such as 2-(nitromethylene)-1,3-  
20 thiazolidine, 2-(nitrochloromethylene)-1,3-thiazolidine, 3-methyl-2-(nitromethylene)-1,3-thiazolidine, 3-methyl-2-(nitrochloromethylene)-1,3-thiazolidine and the like; and when 1-amino-3-propanethiol or 1-ethylamino-3-propanethiol is used, thiazines such as tetrahydro-2-  
25 (nitromethylene)-1,3-thiazine, tetrahydro-2-(nitrochloromethylene)-1,3-thiazine, tetrahydro-3-ethyl-2-(nitromethylene)-1,3-thiazine, tetrahydro-3-ethyl-2-(nitrochloromethylene)-1,3-thiazine and the like; and further  
when 1-amino-4-butanethiol or 1-cyclohexylamino-4-butanethiol is used, thiazepines such as hexahydro-2-(nitro-  
30 methylene)-1,3-thiazepine, hexahydro-2-(nitrochloromethylene)-1,3-thiazepine, hexahydro-3-cyclohexyl-2-(nitromethylene)-1,3-thiazepine, hexahydro-3-cyclohexyl-2-(nitrochloromethylene)-1,3-thiazepine and the like;

respectively.

After completion of the reaction, isolation and purification of the desired product can be done easily by employing suitably such an operation as filtration, concentration, extraction or recrystallization. To describe more specifically by way of example, first after completion of the reaction, the reaction mixture is neutralized with an aqueous solution of mineral acid and, after dilution of the neutralized solution with water, extracted with an organic solvent such as chloroform or dichloromethane. After removal of the solvent from the extract, the crude crystals obtained are recrystallized, whereby a purified desired product can be isolated.

Referring now to Examples, this invention is described in more detail. In each Example, the yield is based on the 2,2,2-trihalo-1-nitroethane compound provided for use.

#### Example 1

Into 50 ml of methanol were added 8.1 g of 1-amino-3-propanethiol and 5.0 g of caustic soda, followed by stirring, to be completely dissolved therein. Then, the mixture was cooled to 0°C. While stirring the solution, a solution of 5.4 g of 2,2,2-trichloro-1-nitroethane diluted in 20 ml of methanol was added dropwise slowly over 15 minutes, and the reaction was carried out for one hour. The reaction was exothermic and the liquid temperature was maintained at lower than 10°C (about 8°C). After the reaction, the reaction mixture was neutralized to pH 7 with 6 N aqueous hydrochloric acid, and then with addition of 50 ml of water, extraction with 100 ml of dichloromethane was repeated four times. The extracts were concentrated to give 2.91 g of tetrahydro-2-(nitromethylene)-1,3-thiazine (yield: 60.1 %).

#### Example 2

An experiment was conducted according to the same procedure as in Example 1 except for using 24.1 g of a 28 wt.% methanolic solution of sodium methoxide in place of  
5 5.0 g of caustic soda. As a result, 3.19 g of tetrahydro-2-(nitromethylene)-1,3-thiazine was obtained (yield: 65.9 %).

#### Example 3

An experiment was conducted according to the same  
10 procedure as in Example 1 except for using a 28 wt.% methanolic solution of sodium methoxide in place of 5.0 g of caustic soda and changing the amount of 1-amino-3-propanethiol employed to 5.5 g. As a result, 2.78 g of tetrahydro-2-(nitromethylene)-1,3-thiazine (yield: 57.4  
15 %) was obtained.

#### Example 4

An experiment was conducted according to the same procedure as in Example 1 except for using 29.2 g of a 30 wt.% methanolic solution of potassium ethoxide in place  
20 of 5.0 g of caustic soda. As a result, 3.21 g of tetrahydro-2-(nitromethylene)-1,3-thiazine was obtained (yield: 66.3 %).

#### Example 5

Into 50 ml of methanol was added 8.1 g of 1-amino-3-  
25 propanethiol, followed by stirring, to be completely dissolved therein. Then, the mixture was cooled to 0°C. While stirring the solution, about 1/3-aliquot of a solution of 5.0 g of caustic soda dissolved in 40 ml of methanol was added dropwise thereinto, and the remainder

of about 2/3-aliquot of the solution and a solution of 5.4 g of 2,2,2-trichloro-1-nitroethane diluted in 20 ml of methanol were added dropwise slowly over 50 minutes, and the reaction was carried out for one hour. During  
5 the dropwise addition, the liquid temperature was maintained at lower than 10°C (about 8°C). After the reaction carried out for one hour, the procedure of the post-treatments as described in Example 1 was followed to obtain 4.20 g of tetrahydro-2-(nitromethylene)-1,3-  
10 thiazine (yield: 86.8 %).

#### Example 6

An experiment was conducted according to the same procedure as in Example 5 except for using 24.1 g of a 28 wt.% methanolic solution of sodium methoxide in place of  
15 a solution of 5.0 g of caustic soda dissolved in 40 ml of methanol. As a result, 4.25 g of tetrahydro-2-(nitromethylene)-1,3-thiazine was obtained (yield: 87.8 %).

#### Example 7

An experiment was conducted according to the same  
20 procedure as in Example 5 except for changing the amount of 1-amino-3-propanethiol employed to 4.1 g. As a result, 3.50 g of tetrahydro-2-(nitromethylene)-1,3-thiazine (yield: 72.3 %) was obtained.

#### Example 8

25 An experiment was conducted according to the same procedure as in Example 5 except for using a solution of 7.0 g of caustic potash dissolved in 60 ml of methanol in place of a solution of 5.0 g of caustic soda dissolved in 40 ml of methanol. As a result, 4.18 g of tetrahydro-2-  
30 (nitromethylene)-1,3-thiazine was obtained (yield: 86.3 %).

## Example 9

An experiment was conducted according to the same procedure as in Example 5 except for using 9.5 g of 2,2,2-tribromo-1-nitroethane in place of 5.4 g of 2,2,2-trichloro-1-nitroethane. As a result, 4.15 g of tetrahydro-2-(nitromethylene)-1,3-thiazine was obtained (yield: 84.4 %).

## Example 10

10 An experiment was conducted according to the same procedure as in Example 5 except for using 6.5 g of 1,2,2,2-tetrachloro-1-nitroethylene in place of 2,2,2-trichloro-1-nitroethane. As a result, 4.0 g of tetrahydro-2-(nitrochloromethylene)-2,3-thiazine was obtained (yield: 81.0 %).

## 15 Example 11

An experiment was conducted according to the same procedure as in Example 4 except for using 6.9 g of 1-amino-2-ethanethiol in place of 1-amino-3-propanethiol. As a result, 3.20 g of 2-(nitromethylene)-1,3-thiazolidine was obtained (yield: 72.4 %).

20

## Example 12

An experiment was conducted according to the same procedure as in Example 5 except for using 9.3 g of 1-amino-4-butanethiol in place of 1-amino-3-propanethiol. As a result, 4.47 g of hexahydro-2-(nitromethylene)-1,3-thiazepine was obtained (yield: 84.9 %).

25

## Example 13

Into 40 ml of methanol were added 5.0 g of 1-methylamino-3-propanethiol and 1.0 g of caustic soda, followed by stirring, to be completely dissolved therein. Then, the mixture was cooled to 0°C. While stirring the solution, a solution of 2.2 g of caustic soda dissolved in 25 ml of methanol and a solution of 3.5 g of 2,2,2-trichloro-1-nitroethane diluted in 20 ml of methanol were added at the same time dropwise slowly over 50 minutes, and the reaction was carried out for one hour. The reaction was exothermic and the liquid temperature was maintained at lower than 10°C (about 8°C). After the reaction, the reaction mixture was neutralized to pH 7 with 3 N aqueous hydrochloric acid, and then with addition of 60 ml of water, extraction with 50 ml of methylene chloride was repeated four times. The extracts were concentrated to give 3.27 g of tetrahydro-3-methyl-2-(nitromethylene)-1,3-thiazine (yield: 94 %).

#### Example 14

An experiment was conducted according to the same procedure as in Example 13 except for using 15.4 g of 28 wt.% methanolic solution of sodium methoxide in place of caustic soda. As a result, 3.31 g of tetrahydro-3-methyl-2-(nitromethylene)-1,3-thiazine (yield: 95 %) was obtained.

#### Example 15

An experiment was conducted according to the same procedure as in Example 13 except for using 5.6 g of 1-ethylamino-3-propanethiol in place of 1-methylamino-3-propanethiol. As a result, 3.53 g of tetrahydro-3-ethyl-2-(nitromethylene)-1,3-thiazine was obtained (yield: 94 %).

## Example 16

An experiment was conducted according to the same procedure as in Example 15 except for using 4.4 g of caustic potash in place of caustic soda. As a result,  
5 3.54 g of tetrahydro-3-ethyl-2-(nitromethylene)-1,3-thiazine (yield: 94 %) was obtained.

## Example 17

An experiment was conducted according to the same procedure as in Example 13 except for using 6.3 g of  
10 1-isopropylamino-3-propanethiol in place of 1-methylamino-3-propanethiol. As a result, 3.80 g of tetrahydro-3-isopropyl-2-(nitromethylene)-1,3-thiazine was obtained (yield: 94 %).

## Example 18

15 An experiment was conducted according to the same procedure as in Example 13 except for using 8.3 g of 1-n-hexylamino-3-propanethiol in place of 1-methylamino-3-propanethiol. As a result, 4.54 g of tetrahydro-3-n-hexyl-2-(nitromethylene)-1,3-thiazine was obtained  
20 (yield: 93 %).

## Example 19

An experiment was conducted according to the same procedure as in Example 13 except for using 8.2 g of  
25 1-cyclohexylamino-3-propanethiol in place of 1-methylamino-3-propanethiol. As a result, 4.55 g of tetrahydro-3-cyclohexyl-2-(nitromethylene)-1,3-thiazine was obtained (yield: 94 %).

## Example 20

Example 19 was repeated except that 18.7 g of a 30 wt.% methanolic solution of potassium methoxide was employed in place of caustic potash. As a result, 4.60 g of  
5 tetrahydro-3-cyclohexyl-2-(nitromethylene)-1,3-thiazine was obtained (yield: 95 %).

## Example 21

An experiment was conducted according to the same procedure as in Example 13 except for using 8.6 g of  
10 1-benzylamino-3-propanethiol in place of 1-methylamino-3-propanethiol. As a result, 4.61 g of tetrahydro-3-benzyl-2-(nitromethylene)-1,3-thiazine was obtained (yield: 92 %).

## Example 22

15 An experiment was conducted according to the same procedure as in Example 13 except for using 6.2 g of 1-allylamino-3-propanethiol in place of 1-methylamino-3-propanethiol. As a result, 3.72 g of tetrahydro-3-allyl-2-(nitromethylene)-1,3-thiazine was obtained  
20 (yield: 93 %).

## Example 23

An experiment was conducted according to the same procedure as in Example 13 except for using 6.1 g of  
1-propargylamino-3-propanethiol in place of 1-methyl-  
25 amino-3-propanethiol. As a result, 3.65 g of tetrahydro-3-propargyl-2-(nitromethylene)-1,3-thiazine was obtained (yield: 92 %).



## Example 24

An experiment was conducted according to the same procedure as in Example 13 except for using 4.3 g of 1-methylamino-2-ethanethiol in place of 1-methylamino-3-propanethiol. As a result, 2.82 g of 3-methyl-2-(nitromethylene)-1,3-thiazolidine was obtained (yield: 88 %).

## Example 25

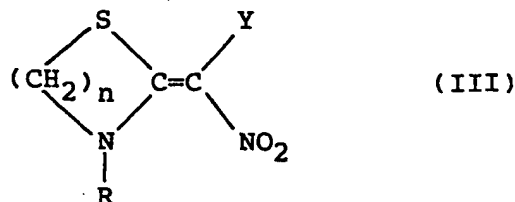
An experiment was conducted according to the same procedure as in Example 13 except for using 5.6 g of 1-methylamino-2-butanethiol in place of 1-methylamino-3-propanethiol. As a result, 3.23 g of hexahydro-3-methyl-2-(nitromethylene)-1,3-thiazepine was obtained (yield: 86 %).

## Example 26

15 An experiment was conducted according to the same procedure as in Example 13 except for using 4.4 g of 2-bromo-2,2-dichloro-1-nitroethane in place of 2,2,2-trichloro-1-nitroethane. As a result, 3.20 g of tetrahydro-3-methyl-2-(nitromethylene)-1,3-thiazine was  
20 obtained (yield: 94 %).

## Claims:

1. A process for producing a heterocyclic compound having a nitromethylene group as the side chain group, of the formula (III):



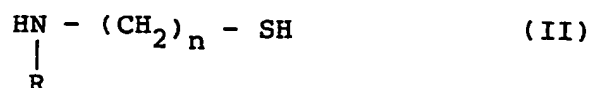
- 5            wherein Y represents a hydrogen atom, a halogen atom or a lower alkyl group, R represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an alkenyl group, an alkynyl group or an acyl group, and n represents an  
 10            integer of 2, 3 or 4,

which comprises reacting a 2,2,2-trihalo-1-nitroethane compound of the formula (I):



- 15            wherein  $\text{X}^1$ ,  $\text{X}^2$  and  $\text{X}^3$  may be the same or different and represent halogen atoms, and Y is as defined above,

with a 1-aminoalkanethiol compound or a 1-N-substituted derivative thereof, of the formula (II):



wherein R is as defined above, and n is as defined above,  
in the presence of a base and in a solvent.

2. The process according to Claim 1, wherein said  
5 halogen atoms represented by  $X^1$ ,  $X^2$ ,  $X^3$  and Y of the compound of the formula (I) are each selected from the group consisting of chlorine, bromine, fluorine and iodine; and said alkyl group represented by Y is an alkyl group having 1 to 4 carbon atoms.
- 10 3. The process according to Claim 1, wherein said alkyl group represented by R of the compound of the formula (II) is an alkyl group having 1 to 12 carbon atoms; said cycloalkyl group is a cycloalkyl group having 5 to 12 carbon atoms; said alkenyl group is an alkenyl  
15 group having 3 to 5 carbon atoms; and said alkynyl group is an alkynyl group having 3 to 5 carbon atoms.
4. The process according to Claim 1, wherein said compound of the formula (II) is used in an amount of from 0.5 to 10 moles per mole of the compound of the formula  
20 (I).
5. The process according to Claim 1, wherein said base is selected from the group consisting of sodium methoxide, sodium ethoxide, potassium methoxide, potassium ethoxide, sodium hydroxide, potassium  
25 hydroxide, calcium hydroxide, barium hydroxide, and magnesium hydroxide.
6. The process according to Claim 5, wherein said base is used in an amount of 3 to 6 moles per mole of the compound of the formula (I).
- 30 7. The process according to Claim 1, wherein said

solvent is selected from the group consisting of methanol, ethanol, i-propanol, n-propanol, i-butanol, n-butanol, water, dimethyl sulfoxide, acetonitrile and dimethylformamide.

- 5     8.     The process according to Claim 1, wherein the reaction is carried out at a temperature of from -10 to 50°C for 0.5 to 10 hours.
9.     The process according to Claim 2, wherein the compound of the formula (I) is selected from the group consisting of 2,2,2-trichloro-1-nitroethane, 2,2,2-  
10     tribromo-1-nitroethane and 1,2,2,2-tetrachloro-1-nitroethane.
10.     The process according to Claim 3, wherein the compound of the formula (II) is selected from the group  
15     consisting of 1-amino-2-ethanethiol, 1-amino-3-propanethiol, 1-amino-4-butanethiol, 1-methylamino-3-propanethiol, 1-methylamino-4-butanethiol, 1-ethylamino-2-ethanethiol, 1-ethylamino-3-propanethiol, 1-isopropyl-  
amino-3-propanethiol, 1-hexylamino-3-propanethiol,  
20     1-cyclohexylamino-3-propanethiol, 1-benzylamino-3-propanethiol, 1-allylamino-3-propanethiol and 1-propargylamino-3-propanethiol.